

SYNTHESIS OF BIS(TRIALKYLSILYL)AMIDE AND COMPOSITION
OBTAINED

The present invention relates to the
synthesis of bis(silyl)amide, more particularly to
5 compositions with a high content of N,O-
bis(trialkylsilyl)amide. The invention relates more
particularly to bis(trialkylsilyl)amides which can be
used as silylating agents.

It is known practice to use bis(silyl)amides
10 as silylating agents which do not give rise to
inorganic salts; these products are particularly
advantageous; reference may be made in particular to
the French patent application published under No.
2,574,078 and entitled: "Process for producing persilyl
15 carboxylic acid amides" [sic].

However, it is extremely difficult to obtain
these compounds with a degree of purity which is
sufficient to make them easy to use. Among the problems
encountered in this use, mention may be made of
20 - the presence of impurity, which reduces the stability
and harms its storage;
- the presence of monosilyl derivative, which makes it
difficult to use since the monosilyl derivative also
has silylating ability, but with different reactivity.
25 This presence is all the more of an inconvenience since
it is difficult to obtain reproducible contents of mono
derivative in the bis d rivative.

The two bis isomers do not have identical reactivity and cannot be separated by physical means.

The problem is further complicated by the great similarity of the physical properties of the monosilyl derivatives with respect to the bis-silyl derivatives. This makes the separation, in particular by distillation, very difficult and often incomplete with laboratory techniques and impracticable on the industrial scale.

10 Accordingly, one of the aims of the present invention is to provide a process for obtaining N,O-bis(silyl)amides.

Another aim of the present invention is to provide a process of the above type for obtaining N,O-bis(silyl)amides directly with a high degree of purity.

15 Another aim of the present invention is to provide a process of the above type for obtaining N,O-bis(silyl)amides directly with a degree of purity at least equal to 90%, advantageously to 95%.

20 Another aim of the present invention is to provide N,O-bis(silyl)amides whose degree of purity is at least equal to 95%, advantageously to 98%.

These aims and others which will become apparent hereinbelow are achieved by means of a process in which the amide is subjected to the action of a trialkylsilyl halide on an amide bearing a group Rf in the presence of a base whose halide, or hydrohalide, is insoluble in the medium and in the presence of a non-

polar and non-hydrophilic solvent.

It is preferable for the solvent to be very sparingly basic and its basicity is assessed with reference to the "donor number".

5 An organic solvent with a donor number not greater than that of cyclohexane is preferably chosen. It is even preferable for it to be too low to be measured! There is no critical nature attached to the lower limit.

10 As regards the requirements relating to the basicity of the organic solvent to be used, it will be recalled that the "donor number", sometimes denoted by the abbreviation "DN", gives an indication as to the nucleophilic nature of the solvent and reveals its
15 ability to donate a lone pair.

 A definition of the "donor number" is found in the book by Christian Reinhardt, [Solvents and Solvent Effects in Organic Chemistry - VCH p. 19 (1988)], which is defined as the negative ($-\Delta H$) of the
20 enthalpy (Kcal/mol) of the interaction between the solvent and antimony pentachloride, in a dilute dichloromethane solution.

 As non-polar solvent, mention should be made of those which have a relative dielectric constant
25 epsilon of not more than 5.

 The said solvent is advantageously such that water has a solubility therein of only 1% at most, preferably 50 ppm.

It is desirable for the said solvent to be such that the reaction mixture fully dissolves the bis(silyl)amide.

The said solvent can be a mixture of various
5 solvents.

It is desirable for the said solvent to be chosen from hydrocarbons, which are advantageously aliphatic and preferably non-cyclic, silanes and fluorohydrocarbons, and mixtures thereof.

10 The said solvent is chosen from those whose (starting) boiling point is, at atmospheric pressure, not more than about 100°C (advantageously two significant figures).

According to one particularly advantageous
15 embodiment of the present invention, the said solvent is chosen from those whose (starting) freezing point is, at atmospheric pressure, not more than 0°C, advantageously not more than -10°C.

As regards the said base, it is
20 advantageously organic. It is desirable for the said base not to be silylable.

According to an advantageous variant of the present invention, the said base is an organic base which contains not more than about 10 (preferably two
25 significant figures) carbon atoms per basic function.

The said base is generally a pnictine.

The term pnictine means hydrocarbon-based trivalent derivatives of the elements from column VB,

of a period at least equal to the second and in general lower than the sixth (the elements nitrogen, phosphorus, arsenic and antimony are more particularly intended) of the Periodic Table of the Elements

5 (supplement to the Bulletin de la Société Chimique de France, January 1966, No. 1). More specifically, they are hydrocarbon-based derivatives of the elements from column V. They are derived from hydrogen pnictides by total or partial substitution of hydrogen with
10 hydrocarbon-based residues which can be alkyl [in the present description ALK-yl is taken in its etymological sense as the hydrocarbon residue of an ALKAN-ol after disregarding the alcohol (or -ol) function] or aryl, connected via a single bond to the atom from column VB.

15 Thus, in the case of nitrogen, the substitution of hydrogen nitride (ammonia) gives amines, in the case of phosphorus, the substitution of hydrogen phosphide gives phosphines, in the case of arsenic, the substitution of hydrogen arsenide gives
20 arsines and in the case of antimony, the substitution of hydrogen antimonide (or stibide) gives stibines.

Thus, the organic bases consisting of hydrocarbon-based derivatives of the elements from column V are advantageously derived from hydrogen
25 pnictides by total or partial substitution of the hydrogen with monovalent hydrocarbon-based residues, advantageously with alkyls [in the present description, ALK-yl is taken in its etymological sense as the

hydrocarbon residue of an ALKAN-ol after disregarding the alcohol (or -ol) function]; these alkyl compounds are, by analogy with the term pnictide, denoted in the present description by the term pnictines.

5 It is desirable for the said base to be an organic base whose conjugate acid is not silylable.

It is preferable for the said base to be an organic base which contains not more than about 10 (preferably two significant figures), preferably not
10 more than 8, atoms (excluding hydrogen) per basic function.

The said base advantageously contains an amine function.

It is preferable for the amine to be at least
15 partially soluble in the said amide, advantageously totally soluble.

The amides mainly targeted are those which have the following formula:



- 20 - with x representing 0 or 1;
- with R_1 , R_2 and R_3 being chosen from alkyl groups containing from 1 to 10 carbon atoms, optionally connected to one of the other groups R_1 , R_2 and R_3 ;
- with R_f (perfluoroalkyl) meaning radicals of formula:



where the identical or different groups X represent a fluorine or a radical of formula C_nF_{2n+1} where n is an integer not greater than 5, preferably not greater than

2;

where p represents an integer not greater than 2;

where EWG represents an electron-withdrawing group

whose functions, if any, are inert under the reaction

5 conditions, advantageously fluorine or a perfluoro
residue of formula C_nF_{2n+1} where n is an integer not
greater than 8, advantageously not greater than 5.

The total number of carbons in Rf is
advantageously between 1 and 10, preferably between 1
10 and 5.

In general, the said amide is an amide chosen
from those of pentafluoropropanoic acid and those of
trifluoroacetic acid.

According to a particularly advantageous
15 embodiment of the present invention, a mixture of y mol
(advantageously y is between x/10 and x/2 mol) of amide
and of trialkylamine (from two y to 5 y equivalents) is
poured onto a feedstock of alkane(s) (C5 to C8) (volume
in the region of one and a half times [from 50 to 250%
20 by volume] the amount of the other reagents) and x mol
of halosilane.

The addition is carried out while keeping the
temperature at the reflux point or close to it. At the
end of the addition, this reflux is maintained for 1
25 hour to one day.

At the end of the reaction, the reaction
medium is cooled to room temperature and the white
precipitate formed is filtered off while maintaining an

in rt and dry atmosphere. The precipitate is washed using a relatively non-polar alkane, advantageously an n-alkane, preferably pentane or hexane.

The non-limiting examples below illustrate
5 the invention.

Example No. 1: Synthesis of
bis(trimethylsilyl)trifluoroacetamide

A mixture of 0.2 mol (22.6 g) of trifluoroacetamide and 0.6 mol (60.6 g) of
10 triethylamine is added to a feedstock of 120 ml of pentane and 0.8 mol (90.4 g) of Me_3SiCl .

The addition is carried out at a flow rate of 14 ml/h while keeping the temperature at the reflux point. At the end of the addition, this reflux is
15 maintained for 11 hours 30 min.

At the end of the reaction, the reaction medium is cooled to 20°C and the white precipitate formed is filtered off, while maintaining an inert and dry atmosphere. The precipitate is washed with pentane.

20 The filtrate is distilled rapidly to remove the reaction solvent (pentane). The residue is then rectified on a 10-theoretical-plate column.

The bis derivative is thus isolated (boiling at 59.6°C - 60.1°C at 60 mbar) with a DC relative to
25 the acetamide of 100% and a selectivity towards bis(trimethylsilyl)trifluoroacetamide of 89%. The purity of the sample is greater than 99.5%.

Example No. 2: Role of the solvent

Identical to Example 1, except than hexane is used as solvent.

The rectified bis(trimethylsilyl)trifluoro-
5 acetamide is obtained with a DC of 100% and a selectivity of 95%.

Example No. 3: Use of other amines

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| Dura- tion (hrs) | $\phi^{\circ}\text{C}$ | Solvent | Amine | DC/ acet- amide | RY/ bis deri- vative | RY/ mono deri- vative |
|------------------------|------------------------|---------|--------------------------------------------------|-----------------------|-------------------------------|--------------------------------|
| 11.30 | 47 | pentane | Et_3N | 100 | 98 | 2 |
| 16 | 68 | - | HMDZ+ Et_3N | 100 | 50 | 50 |
| 3 | 50 | pentane | $\text{Bu}_3\text{N}^{(a)} (**)$ | 100 | 0 (25) | 0 (75) |
| 14 | 70 | HMDZ | pyridine | 100 | 0 | 100 |
| 3 | 50 | pentane | diiso- propyl- ethyl- amine (a) (**) | 100 | 0 (25) | 0 (75) |
| 3 | 50 | pentane | Oct_3N (a) | 100 | 0 | 0 |
| 3 | 60 | - | HMDZ | 100 | 0 | 100 |

* temperature

(a) At the end of the addition of the amide + t rtiary

amine mixture, the presenc of mono- and bis(trimethylsilyl)trifluoroacetamide is observed, which disappears over time.

- 5 (**) At the end of the addition of the amide + tertiary amine mixture, the RY of bis derivative is about 25% and the RY of mono derivative is 75% - result obtained by GC analysis.